

THERMAL BLACK FORMATION  
DURING DESTRUCTION OF LIQUID WASTES  
BY SUBMERGED ARCS

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ABSTRACT

Submerged, electrical arc discharges are an effective means for destruction and minimization of liquid wastes. Solutions of wastes, or waste liquids, are pyrolyzed by the arc to form gases, solid thermal blacks, and inorganic precipitates. This paper reports on an investigation of the thermal blacks produced by a specific submerged arc technology. With this process, multiple arcs are struck at the interface between an insulating organic oil phase and a conducting water phase. The high temperatures of the arc causes fast thermal pyrolysis of the adjacent organic material to occur in the presence of water vapor.

Three different organic phases were investigated; heptane, diesel fuel, and toluene. The thermal blacks produced by these different organic liquids were subjected to elemental analyses and found to be distinctly different in their ratio of carbon to hydrogen and carbon to oxygen. These differences may reflect the mechanisms by which the graphite structures form from the different types of organic feed stocks.

Introduction

The Al-Chem Detoxifier is a patented process being developed to treat liquid wastes. This technology creates an electrical arc discharge at a submerged oil-water interface. The high temperature of the electrical arc causes fast pyrolyses of the oil phase in the presence of water. Hence, the oil, water and any soluble waste organics dissolved in either phase are destroyed. A predominately hydrocarbon gas phases is produced and withdrawn from the unit. Inorganic precipitates and a suspension of solid thermal blacks also form. The thermal blacks are particularly troublesome, since they are electrically conductive and remain suspended in the organic phase. At some point during the operation, their concentration level becomes sufficient to cause a short of the high electrical potential needed to produce the arc discharge. At this point the unit fails to function. Hence the initial studies with the Al-Chem Detoxifier have been directed at the thermal-black formation process and potential methodologies for abatement.

Three different types of hydrocarbon liquids were used in the studies on thermal black formation. Heptane was selected to represent aliphatic liquids. Diesel fuel represented naphthenic structure and toluene the liquid aromatics. The heptane and

toluene were pure liquids compared to diesel and gasoline which are blends of hydrocarbons and have relative octane ratings and volatilities. However, they are also more typical of the organic solvents associated with waste liquids to be treated for disposal in later demonstrations.

#### EXPERIMENT APPROACH

The different organic liquids were charged to bench scale Al-Chem Detoxifier units. The operation and description of these units are described in other publications.

(1) (2) (3) (4). These small units were operated for periods of four to twelve hours. During this period, samples of the pyrolysis gases formed were collected for analyses.

After the run was completed, the thermal blacks which had been generated were filtered through a 10 micron filter, then dried. The dried thermal black was then subjected to elemental analyses and in some cases examined microscopically with ESM. The better ESM studies, however, were obtained by passing dilute suspensions of the organic liquid with its thermal black through 5 micron millipore filters, then subjecting the filter medium to ESM. The elemental analysis, gas analysis, and ESM work were all done at commercial laboratories on a fee basis.

#### DISCUSSION OF RESULTS: GASES

The composition of the gases formed during the pyrolysis process are shown in Table 1, except for toluene. Gases produced with this liquid hydrocarbon feed have yet to be analyzed. The gas compositions are shown primarily as a means of providing insights into the pyrolysis process and the subsequent formation of the thermal blacks.

Typical of any pyrolytic process for hydrocarbons which takes place at elevated temperatures, hydrogen and unsaturated hydrocarbons were produced in abundance. Since water was present in our process, carbon monoxide and dioxide were also formed. With the Al-Chem apparatus, the electric arc probably exceeds 2000°C. However, because the arc discharge zone is small relative to the bulk volume of the unit, the bulk temperature of surrounding liquids is limited to 70°C. This means that products of the pyrolysis reaction are quickly quenched and cannot reach a thermodynamic equilibrium at the arc temperature. Hence acetylene, which is unstable at 70°C based on thermodynamic considerations, remains an abundant species of the gases produced. However, with the aliphatic hydrocarbon liquids, it is the acetylene which is suspected as being a major source of the thermal blacks formed.

While the n-heptane and gasoline show similar trends in gas compositions, the gasoline produced significantly more of the heavier C<sub>5</sub> vapors. This was felt to be due to the lighter hydrocarbons added to the gasoline to increase volatility. At

70°C these light hydrocarbons were being stripped from the gasoline without being subjected to the pyrolytic action of the transfer arc. The diesel fuel, representative of naphthenic hydrocarbons gave a different distribution of product gases. These saturated ring structures produced more hydrogen and oxides of carbon than the aliphatic hydrocarbon liquids. In the case of the naphthenic hydrocarbons, therefore, it is postulated that the graphitic thermal blacks are generated by combination of modified ring structures already present in the liquid hydrocarbon feeds. Similar behavior appears to take place with the aromatic hydrocarbon feed stocks. The aliphatic liquid hydrocarbons, however, must form ring structures from unsaturated acetylenes or alkenes prior to thermal black formation..

#### SOLIDS

The information shown in Table 2 summarizes the various aspects of the thermal blacks formed. The diesel, representing the naphthenic liquid hydrocarbons, forms the greatest amount of thermal black per unit of power input. The data for toluene are missing, but it too is expected to show a rather significant production of thermal black for power input. The remainder of the table shows the chemical make up of the thermal blacks with respect to their carbon, hydrogen and oxygen contents. Although small amounts of nitrogen and ash appeared during the analyses of the thermal blacks, these were discarded in later calculations. Of the organic liquids which were run, the gasoline gave the greater variation. This was attributed again to the nature of gasolines as blends of various liquid hydrocarbons to produce the desired octane and volatility characteristics. A summary of these data indicate the following possible orders for the atomic ratios for the thermal blacks formed.

C/H Molar ratio	aromatic > aliphatic > naphthamics
C/O Molar ratio	aromatic > naphthenic > aliphatic

The carbon to hydrogen ratio speaks both to the type of feed stock organic used and to the mechanism by which the thermal blacks are formed. Aromatics have higher C/H ratio to begin with, and their unsaturated, stable rings can polymerize to the thermal black structure by hydrogen losses and free radical formation on the rings. The free radicals then terminate through combination mechanisms. Naphthenic feedstocks need not lose as much hydrogen to proceed through this polymerization process. Aliphatic materials must lose proportionately more hydrogen to become sufficiently unsaturated (acetylene) prior to formation of cyclic rings rather than linear or brached thermal blacks.

The carbon to oxygen ratio on the other hand speaks to the degree to which oxygen apparently takes part in ring structures and the termination of the free radicals. Oxygen is known to form both stable five membered (ether) rings with carbon and to suppress free radical polymerization processes. In either case the order shown in Table 2 was not unexpected.

Finally a potential chemical formula for high color channel black of a commercial variety is shown in Table 2.(5) This suggests that in comparison to commercial thermal blacks, those produced by the Al-Chem Detoxifier have approximately the same oxygen content but considerably more hydrogen. This may well reflect the nature of the submerged arc pyrolysis process in which free radicals are generated and then abide in the hydrogen rich medium of the liquid hydrocarbon where transfer processes represent a termination procedure.

#### SUMMARY

Thermal blacks produced by submerged electrical transfer arcs in the presence of water have chemical structures characteristic of the liquid hydrocarbon feedstocks from which they are produced. Although these thermal blacks have much the same physical characteristics as commercial thermal blacks, they are much richer in hydrogen content. This suggests that they are not quite the same polyaromatic or graphitic type structures as commercial thermal blacks.

#### BIBLIOGRAPHY

1. Don Ethington, Ray J. Riley, Richard W. Tock, "Method for Gas Synthesis", U.S. Patent Number 4, 690, 743, September 1, 1987.
2. R.W. Tock, H.W. Parker, M. Shafi, and D. Ethington, "Mass and Energy Balances Around Electrical Discharges at Oil-Water Interfaces," ASME/JSME Thermal Engineering Conference, Volume 2, 595-599. Editors P.J. Marto and I. Tanasawa, 1987.
3. Richard William Tock and Don Ethington, "Small-Scale Disposal of Agrichemicals," AIChE Symposium Series, Heat Transfer, 413-417, Pittsburgh, 1987.
4. Richard William Tock and Don Ethington, "Transfer Plasmas Destroy PCB Fluids," Chemical Engineering Comm., Volume 71, 177-187, 1988.
5. Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd Edition, Volume 4, 243-282, Interscience John Wiley and Sons, 1964.

TABLE 1

## GAS PHASE COMPOSITIONS FOR DIFFERENT FEEDSTOCKS

Feed Liquids

<u>Oil Phase</u>	<u>n-Heptane</u>	<u>Diesel</u>	<u>Gasoline</u>
<u>Water Phase</u>	<u>Tap Water</u>	<u>Tap Water</u>	<u>Tap Water*</u>
Component	Mole percent		
Hydrogen (H <sub>2</sub> )	56.4	63.9	41.8
Carbon Monoxide (CO)	12.7	17.0	11.3
Acetylene (C <sub>2</sub> H <sub>2</sub> )	11.4	6.3	5.6
Ethylene (C <sub>2</sub> H <sub>4</sub> )	7.9	2.3	2.7
Methane (CH <sub>4</sub> )	4.3	2.5	3.0
Pentene +(C <sub>5</sub> =+)	3.0	3.5	18.0
Carbondioxide (CO <sub>2</sub> )	0.9	3.2	1.3
Propylene (C <sub>3</sub> H <sub>6</sub> )	1.2	0.6	1.43
Misc. (Hydrocarbons)**	2.2	0.7	15.0

\*Tap water contained 0.5M hydroquinone

\*\*Predominatley unsaturated hydrocarbons

TABLE 2  
CARBON BLACK ANALYSES FOR EXPERIMENTAL RUNDS

		Organic Hydrocarbon Phase			
		<u>Heptane</u>	<u>Gasoline</u>	<u>Diesel</u>	<u>Toluene</u>
Thermal Black Formation Rate (gram/kw hr)		12.53	3.64	41.38	--
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Atomic Weight %	C	86.33%	85.76-92.15%	87.01-82.76%	93.59%
	H	3.23%	2.57-03.17%	7.61-10.82%	1.38%
	O	10.42%	11.66-04.67%	5.42-06.45%	5.03%
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Possible Molecular Formula		C <sub>11</sub> H <sub>5</sub> O	C <sub>11</sub> H <sub>4</sub> O or C <sub>26</sub> H <sub>11</sub> O	C <sub>21</sub> H <sub>22</sub> O or C <sub>17</sub> H <sub>27</sub> O	C <sub>25</sub> H <sub>4</sub> O
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C/H Molar Ratio		2.2	2.95-2.36	0.95-0.63	6.25
C/O Molar Ratio		11.0	11.0 -26	17 - 21	25
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Commercial high -color channel blacks

Molecular Formula C<sub>37</sub>H<sub>2</sub>O<sub>3</sub>    C/H = 18.5    C/O = 12.3